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Laser Induced Breakdown Spectroscopy for Rapid Delineation of Metals in Soils

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ABSTRACT

The development of a metal sensor that can be deployed with a cone penetrometer for in-situ subsurface measurements is described. The sensor utilizes Laser Induced Breakdown Spectroscopy (LIBS) to analyze the atomic emission of metals on contaminated soil samples. The novel approach taken in this work is that the measurements are done remotely with both laser excitation and signal collection transmitted through fiber optic cables.

INTRODUCTION

The cone penetrometer system has been used as a platform for the deployment of underground sensors for many years. Until recently, these sensors have been aimed primarily at gathering information related to soil strength characteristics. In the last five years the utility of the cone penetrometer has been expanded by the development of fiber optic chemical sensors using fluorescence based techniques for the in-situ measurement of petroleum, oils and lubricants (POLs)[1]. The cone penetrometer is now gaining acceptance as a rapid, low cost tool for delineation of POL plumes at hazardous waste sites. The utility of the cone penetrometer as a site characterization tool would be enhanced if the array of sensors available via the cone penetrometer platform were further expanded. In the current work, we demonstrate laboratory operation of a fiber optic sensor suitable for cone penetrometer deployment that is designed to detect the presence of heavy metals in-situ. The sensor exploits the technique of Laser Induced Breakdown Spectroscopy (LIBS) to detect metals in soil at the sub ppm level.

The LIBS method has been used previously for the identification and quantification of elemental species in solids, liquids and gases[2] and recent work has examined the application of LIBS to metal contaminated soil[3]. The conventional LIBS technique involves the use of a high power pulsed laser that is focused to a small spot on a sample to generate a high power density of several GW/cm^2 or higher. In the region of the focused spot, the high power density of the laser pulse results in the rapid heating, vaporization and ionization of a small quantity of material. Thus, a laser induced plasma is formed which emits light that can be monitored to provide information about the plasma's elemental constituents.

The time resolved emission of the plasma is characterized by an initial broadband continuum that is due to recombination of electrons and ions and plasma interactions such as Bremsstrahlung. As the plasma cools, this broadband background decays rapidly leaving only longer lived spontaneous emission lines at discrete wavelengths that are characteristic of the elemental species present within the plasma.

Since these emission lines generally outlive the continuum emission, they can be temporally resolved by appropriately time gating the optical detector that is monitoring the plasma. In practice, a short, high voltage gate pulse is applied to the detector that makes it light sensitive only after the broadband emission has ceased. The elemental emission of interest is then integrated by the detector until the signal has decayed away. In this way the unwanted continuum background can be separated from the elemental emission to provide a signal that is optimized at the emission line of the elemental species of interest.

The LIBS technique has several features which make it well suited to deployment in a cone penetrometer probe. The spontaneous elemental emission is characterized by a narrow linewidth and there is a choice of several spectral lines from a given element, so LIBS is sufficiently specific that background interferences are minimal. Additionally, the fact that all the species present in the focal volume enter the plasma together allows for simultaneous multicomponent analysis. Since the spectral results are available immediately, analysis of the results and site delineation decisions can be carried out in real time. Another crucial point for cone penetrometer deployment is that the technique requires no sample preparation so it is suitable for an in-situ probe.

The approach to LIBS that will be explored in the current work is that of performing the measurement remotely over fiber optic cables. The task of delivering the required laser power density to the sample over optical fiber is an obvious concern that has limited enthusiasm in fiber optic LIBS, since it is well known that the transmission capabilities of currently available optical fibers are not without limit. What we intend to demonstrate here is that the power density required on typical soils to initiate laser induced breakdown is sufficiently low that fiber optic LIBS is feasible. Since optical fiber, which will be the principle component of the planned probe, is economically priced, a fiber optic LIBS probe has the added benefit that it will be relatively inexpensive. An inexpensive probe design is important in cone penetrometer work because of the real risk that the probe will be broken and lost while deep underground.

EXPERIMENTAL

The experimental setup used in this work to simulate the essential elements of a LIBS based cone penetrometer probe is shown in Figure 1. The laser used was a Continuum NY61 Nd:YAG laser operating at 1064nm at 10 Hz with a pulsewidth of 20ns. The linearly polarized laser output was varied while maintaining a constant pulsewidth by the use of a halfwaveplate and beamsplitter arrangement mounted on the laser bench. The laser energy was monitored by the use of a beamsplitter to divert part of the beam to an energy meter. The majority (95%) of the laser light passed through the beamsplitter and was focused onto the face of a single 600 micron fused silica core fused silica clad high OH⁻ optical fiber from Polymicro Technologies. The focusing lens used for fiber input was plano convex with a 20cm focal length. The fiber was positioned beyond the focal point of the lens so that the diameter of the beam on the fiber face was 500 microns. The laser light passed through the excitation fiber and was reflected by a dichroic mirror that was highly reflecting at 1064nm and highly transparent from 400-600nm. The excitation beam was focused by an f-number 0.63 aspheric lens onto a soil sample that was spiked with known quantities of a selected metal. The output energy of the fiber could be measured directly with a second energy meter by removing the dichrioc mirror. The spot size at the sample was calculated to be 200 microns.

Because the elemental emission from the metal contaminant on the vaporized soil sample was at a shorter wavelength (405.78nm) than the excitation wavelength it could be collected by the aspheric lens and focused through the dichroic mirror onto a 10m long bundle of five fibers. The output of the five fiber bundle was arranged in a line and focused and f/# matched onto the input slit of a Spex 750M spectrometer. The spectrometer dispersed the spark emission over an EG&G 1420 gated intensified linear photodiode array (PDA). The PDA detector was controlled by an EG&G 1460 optical multichannel analyzer system. The timing of the detector gate was slaved to the sync pulse from the laser. The duration of the detector time gate pulse was 1 microsecond and it was applied after the broadband background light had decayed.

It was observed that the spark incident on the soil sample during the measurement created a significant shock that effectively displaced sand from the focal region of the aspheric lens. This variation of the soil surface position with respect to the focal point of the lens had the effect of varying the power density at the sample significantly. In order to insure that a new sample was presented to the detector for each laser shot and to minimize the variation of the sample position with respect to the focal point of the aspheric lens, the soil sample was rotated on a turntable and simultaneously agitated. Typically the emission spectra from 1000 sparks were accumulated. This experimental procedure had the desired effects of reducing shot to shot variations in system response due to soil displacement and presenting a larger volume of sample to the detector for averaging of spatial inhomogeneities.

RESULTS AND DISCUSSION

The feasibility of making a fiber optic LIBS sensor for metals on soil depends on the threshold of initiation of a laser induced spark on soil. In order to estimate the initiation threshold on typical soils, five representative natural soils from sites in the US were examined in addition to a standard sea sand available from Fisher. The naturally occurring soils were obtained during field operations of the US Navy Site Characterization and Analysis Penetrometer System and originated at Guadalupe CA, Coronado Island CA, Yuma AZ, Alameda NAS CA and Camp Pendleton CA. For these samples the observed spark initiation threshold power density was $0.5GW/cm^2$, independent of soil type. The power density was calculated by using the measured laser energy and pulsewidth in addition to the laser spot size which was measured with a CCD based Spiricon Laser Beam Analyzer. The criteria for the definition of the spark threshold used here was the visual occurrence of a spark on 100% of the laser shots.

All the metal spiked soil data shown here was gathered using fiber optic excitation and fiber optic collection. The data was gathered using power densities on the input face of the fiber well below the highest values published for fused silica fibers thus far[4] (a few GW/cm^2, depending on surface treatment) to insure the robustness of the sensor. Figure 2 depicts the linearity of the fiber transmission for output energies exceeding 20 mJ for 20ns pulses at 1064nm. The fiber used for this data was 60m long with a 600 micron core. The linear response indicates that the attenuation of the fiber is not dominated by nonlinear effects even for high power densities. The upper end of the curve corresponds to an input power density in excess of 1 GW/cm^2. By using the short focal length aspheric lens shown in Figure 1, the output of the excitation fiber was imaged to 1/3 of the core size or about 200 microns. Because the power density is proportional to the square of the spot size, this reduction in spot size translates to a 9-fold increase in the power density at the sample over the power density present in the fiber. This means that the spark initiation threshold observed on the soil of .5GW/cm^2 can be exceeded by a factor of 18 by the excitation energy possible from just one fiber. If necessary, the sensor could include multiple excitation fibers.

Although LIBS can be used to detect a variety of metals, the approach taken in this work was to use a single metal, Pb, as a representative contaminant on soil samples to evaluate the suitability of the technique as a cone penetrometer sensor. The approach used here can be expanded to other metals with varying sensitivity depending on the strength of the emission lines monitored. Pb contaminated sand samples were prepared by adding measured quantities of aqueous lead acetate to 25g of standard Fisher sea sand. The resulting slurry was tumbled for 24 hours and air dried. Concentrations of 0,10,100,1000, and 10,000 ppm were prepared in this manner. The LIBS measurement was made while the samples were spun and agitated on the turntable shown in Figure 1.

The background corrected response of the system for concentrations of Pb on sand from 0 to 10,000 ppm is shown in Figure 3. The data was gathered at an excitation energy of 7.2 mJ, well below the damage threshold of the fiber. In all the sensor data shown here each spectrum is the result of a 1000 shot accumulation. The Pb emission line at 405.78nm is clearly discernible even at the 10 ppm concentration. Figure 4 shows a plot of the spectrum without background correction on an expanded scale. The peak at 405.78nm in clean sand suggests that there is a small quantity of background Pb in the sand matrix. The background Pb peak has an amplitude of roughly 10,000 counts.

Figure 5 shows a calibration curve for the sensor. The detector response of 10,000 counts in unspiked Fisher sea sand corresponds to a concentration of 0.3ppm for the Pb background. Based on the calibration curve an addition of .3ppm Pb to the soil (twice the background) is clearly visible. This is a conservative estimate of the detection capability of the sensor for the dry sand matrix since the response of the system scales with excitation power density. Because the sensor has been operated far from the damage threshold of the fiber and since the sensor could include multiple excitation fibers, the excitation energy could be increased substantially which would improve the detection limit. At this point in the development of the sensor it is premature to speak in terms of the absolute detection limit since this work is ongoing and several issues regarding matrix effects and excitation energy have yet to be resolved.

The dependence of the sensor on excitation power is shown in Figures 6 and 7. The Pb emission line at 405.78nm was bracketed by additional background lines due to iron present in the standard Fisher sea sand at 404.57nm, 406.32nm and 407.14nm. The sample power density was varied from a value corresponding to the spark initiation threshold up to a value corresponding to three times the spark initiation threshold. A nonlinear benefit from increased excitation power density is evident. Extrapolation of this trend implies that increasing the excitation energy either in a single fiber or by the use of multiple fibers will lead to a similar nonlinear benefit in the detection capability of the system.

Still to be resolved in this study is the issue of matrix effects. Previous work with fiber optic POL sensors in soil has shown that soil type and water content are important calibration issues for in-situ analysis[5]. The soil type effect on the fiber optic LIBS probe is an issue for future consideration and is not addressed in this study. Based on the previous fiber optic POL sensor studies, it is anticipated that finer grain materials with larger surface areas per unit volume for contaminant distribution will reduce the amount of contaminant accessible to a LIBS probe. Therefore, the response of the sensor is expected to be lower in high surface area materials such as clays and higher in low surface area materials such as sands. Because water present in the soil must be vaporized prior to spark ignition, it is intuitive that increasing amounts of water in the soil will lead to lower temperature LIBS plasmas and less sample emission. However, LIBS measurements are routinely made in aqueous solutions so LIBS measurements in contaminated soil in the presence of water are feasible. This is because such a small volume of sample is actually vaporized at the focal region of the excitation lens during a LIBS measurement that only a small quantity of water is present in the plasma region. A preliminary investigation of the variation in system response as a function of the water content of Fisher sea sand is shown in Figure 8. The data is expressed as percent water saturation. It was observed that for the Fisher sea sand used in this work, 6 grams of water was required to fill the interstitial space in a 25 gram sample of sand so the definition used here for 100% saturation is 6 grams water to 25 grams sand. As expected, the data indicates that the energy required to vaporize increasing amounts of water leaves less energy for soil and contaminant vaporization This reduction in available excitation energy effectively pushes the operation of the sensor closer to the spark initiation threshold, so the response of the sensor drops off. As shown in Figure 9, however, the Pb line is still detectable even for 100% saturation. This suggests that the sensor can be calibrated to account for water content. It is essential to note that it is because the data shown here were gathered at a low excitation energy, near the spark initiation threshold, that the effect of water content is so strong. By using a higher power density at the sample to initiate the plasma, the vaporization of the water present in the sample will require a smaller fraction of the total excitation energy and it is expected that the effect of water content on sensor response will be reduced. Additionally, the data on the nonlinear increase in system response as a function of excitation power implies that the relative effect of water content will also be reduced in a nonlinear fashion with increasing sample power density.

CONCLUSION

We have begun the development of a fiber optic based LIBS sensor for the cone penetrometer system and have demonstrated that the fiber optic LIBS technique is suitably sensitive for detection of Pb on dry sand at sub ppm concentrations. The technique developed here for detection of Pb on contaminated sand can also be extrapolated to the detection of other metals. Additionally, the length of

fiber over which this detection method is feasible is appropriate to application to the cone penetrometer and the configuration of the sensor used was robust in the sense that it was operated far below the damage threshold of the laser delivery fiber.

The impact of matrix effects on the response of the sensor will define the required sample power density in the planned cone penetrometer probe. It is expected that at higher excitation energies the effect of water on the sensor response will be reduced. Future work is planned to examine the relationship of excitation power density to this water matrix effect and to investigate the impact of soil type and grain size on the sensor response.

ACKNOWLEDGMENTS

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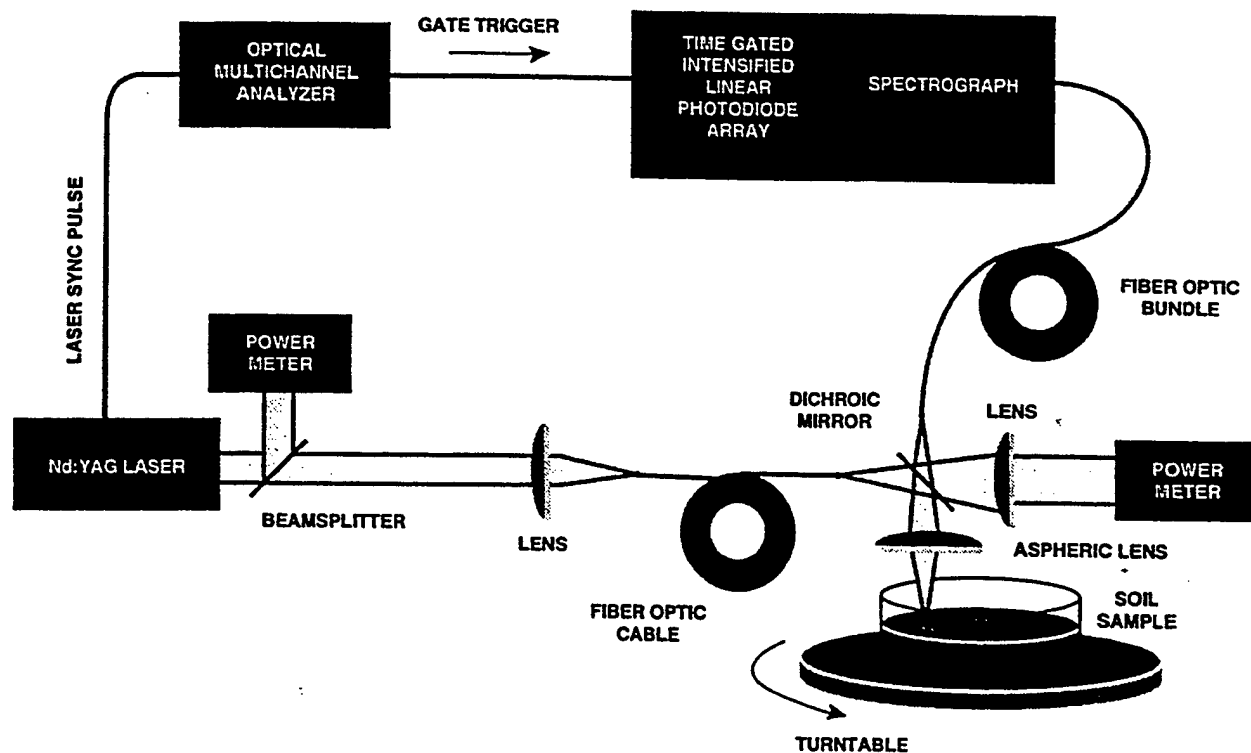
Figure 1. Schematic of Laboratory Fiber Optic LIBS System.
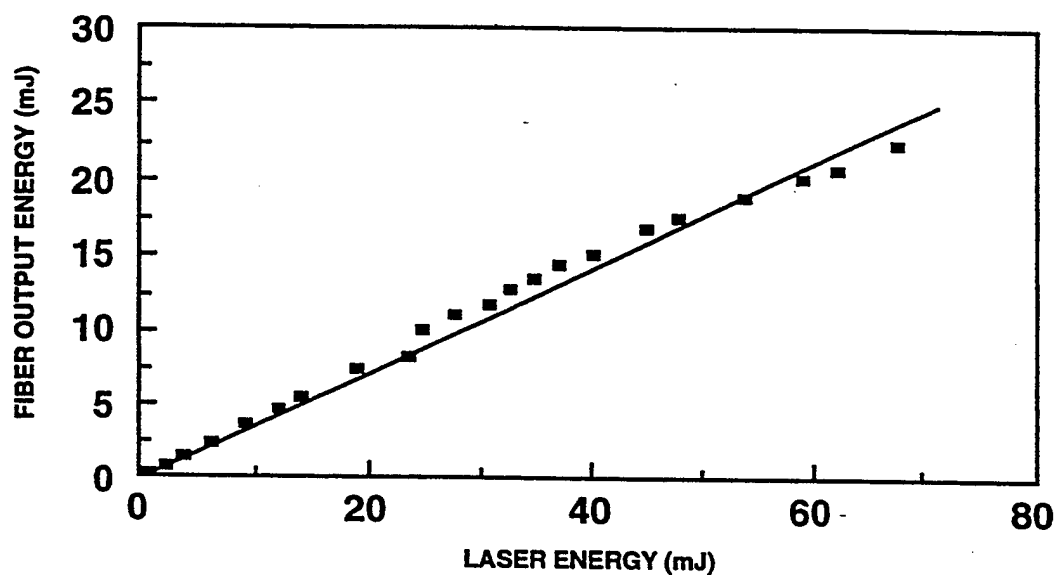

Figure 2. Typical energy deliverable by a single fused silica core, fused silica clad fiber. The fiber used was 60 meters in length with a 600 micron core. More than 20 millijoules is available from a single fiber with no nonlinear attenuation evident. The data is uncorrected for input coupling.
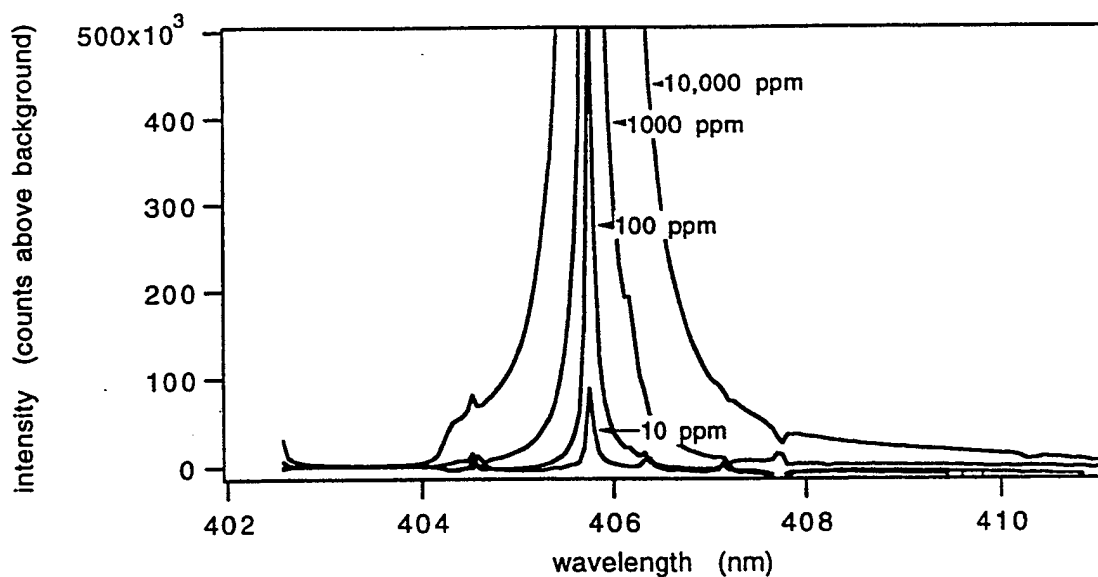
Figure 3. LIBS spectra of various concentrations of Pb on sand. The pulse energy
was 7.2 mJ and 1000 shots were accumulated during these measurements. The data have
been background corrected by subtracting the spectrum measured on an unspiked sample.
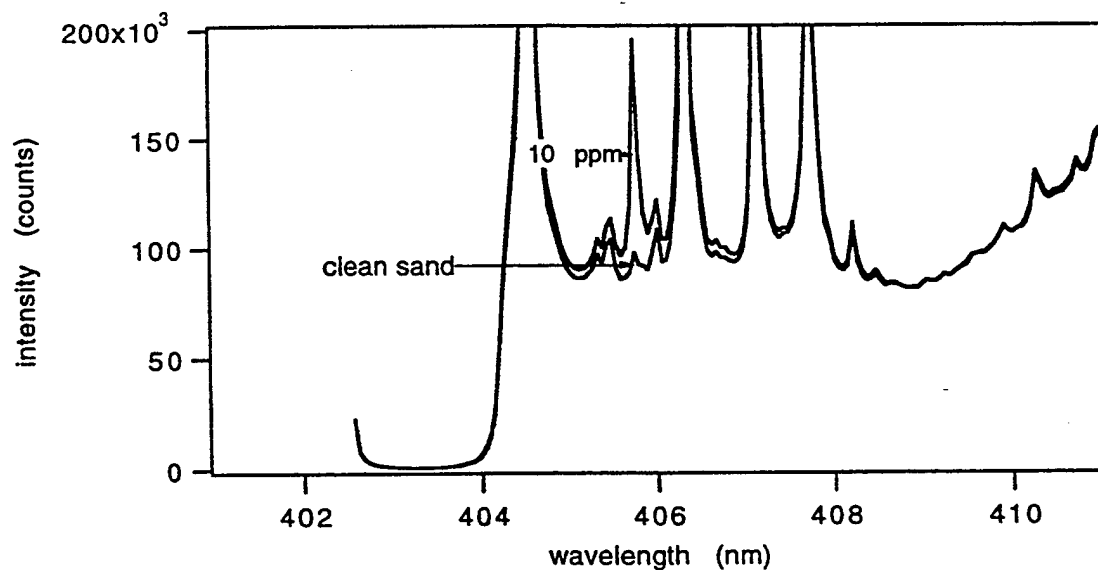
Figure 4. LIBS spectra for Pb on sand without background correction showing
Pb peak for 10 ppm sample. The small peak (approx. 10,000 counts) in the unspiked
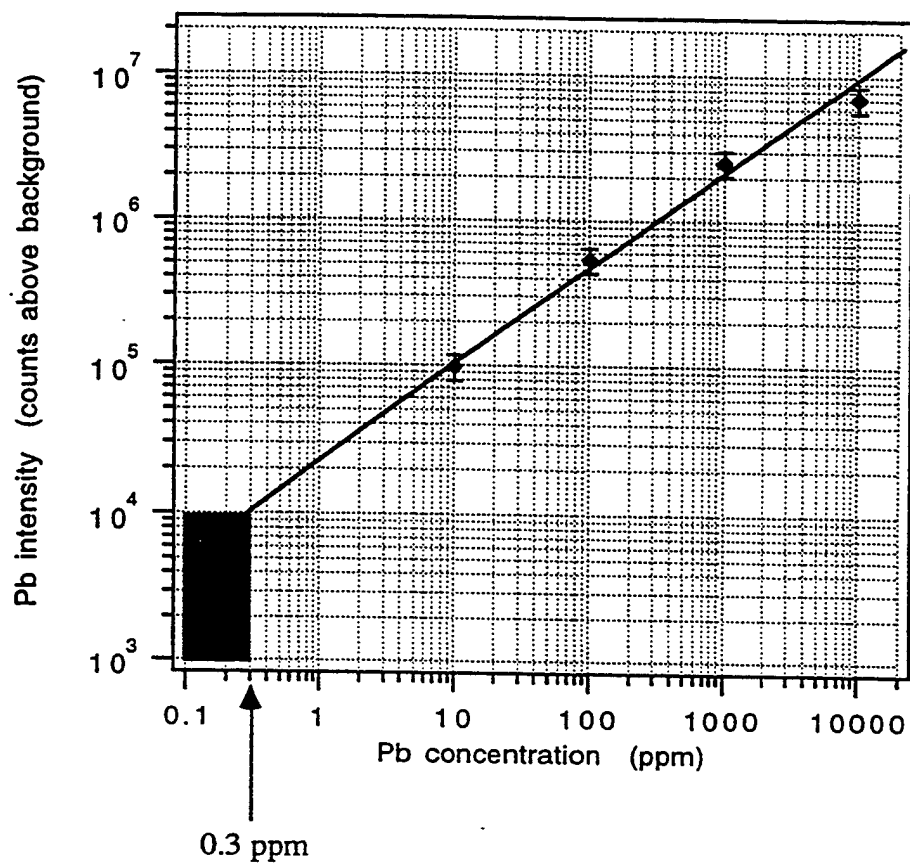sample suggests there may be a small amount of Pb in the clean sand.

Figure 5. Pb signal vs concentration (by weight) using dry Fisher sea
sand as the matrix material. The 10,000 count background
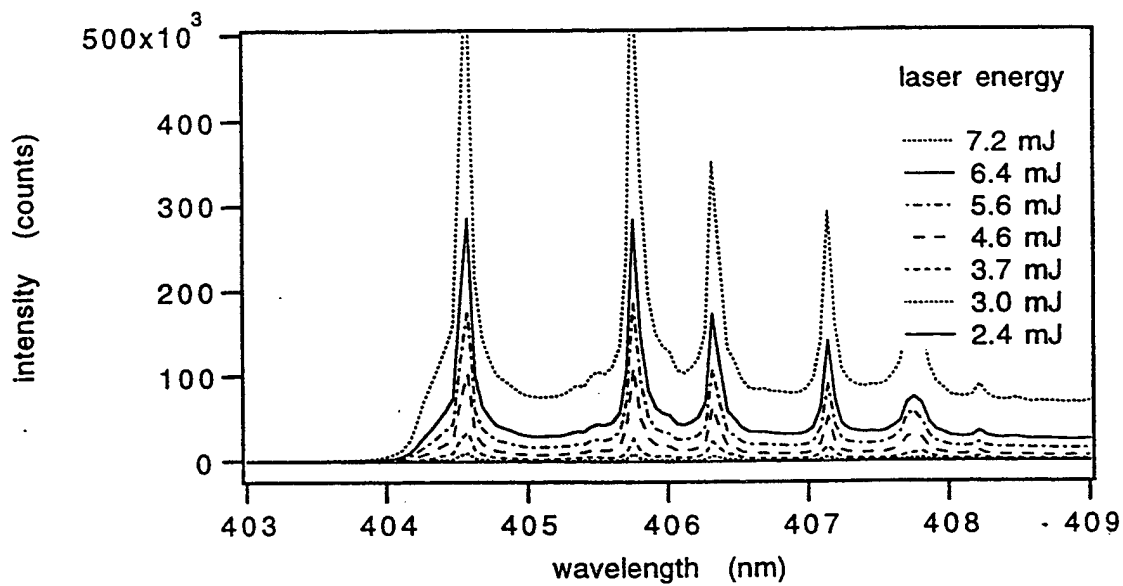in unspiked sand corresponds to a concentration of
0.3 ppm of Pb.

Figure 6. LIBS spectra of Pb on sand for various excitation energies. The concentration used was 100 ppm Pb. Each spectrum is an accumulation of 1000 shots.
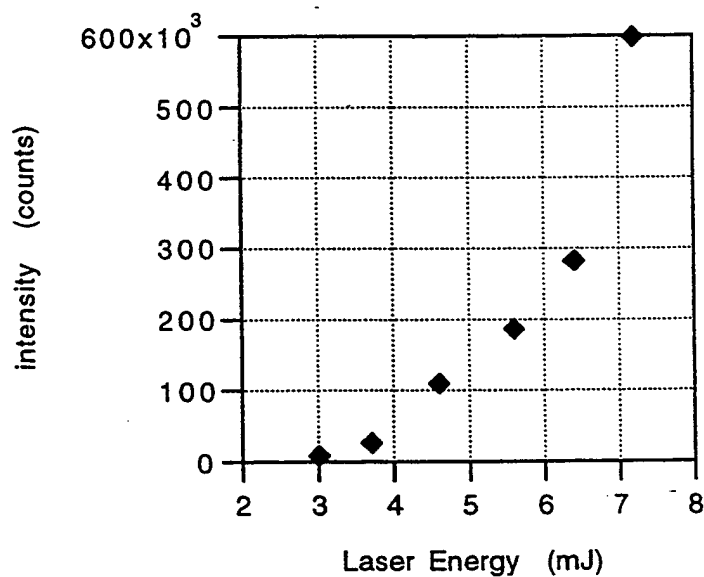

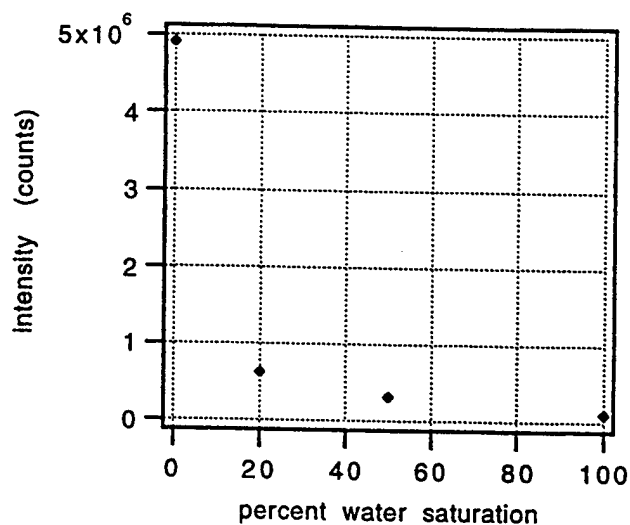Figure 7. LIBS sensor response vs. laser excitation energy.

Figure 8. LIBS sensor response as a function of the water content of the sand. The Pb concentration was 10,000 ppm. Each point represents the intensity of the 405.78 nm Pb line using 1000 shot accumulation and 10 mJ excitation energy.
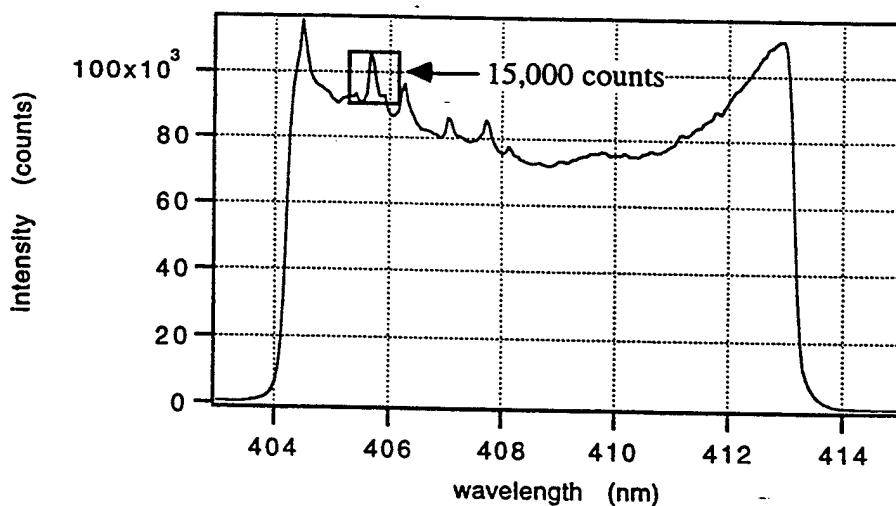

Figure 9. The emission spectrum of Pb on 100% water saturated sand. The Pb emission peak is still visible in the fully saturated sample. (1000 shot accumulation, 10 mJ excitation energy).